

UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2015/2016

TITLE OF PAPER: **ADVANCED INORGANIC**
 CHEMISTRY

COURSE NUMBER: **C401**

TIME ALLOWED: **THREE (3) HOURS**

INSTRUCTIONS: **THERE ARE SIX (6) QUESTIONS.**
 ANSWER ANY FOUR (4) QUESTIONS.
 EACH QUESTION IS WORTH 25
 MARKS.

A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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QUESTION ONE

- (a) Determine the specified quantity:
- The metal-metal bond order consistent with the 18-electron rule for $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2^{2-}$.
 - The identity of the first row-transition metal in $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ (assume a single M-M bond), an 18-electron molecule.
 - The expected charge on $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^z$ on the basis of the 18-electron rule. [3]
- (b) Explain why $\text{V}(\text{CO})_6$ is easily reduced to the monoanion, $[\text{V}(\text{CO})_6]^-$ [4]
- (c) Identify the following reactions by type and predict the products:
- $\text{Re}_2(\text{CO})_{10} + \text{Na/Hg} \rightarrow$
 - $\text{Rh}(\text{PPh}_3)_3\text{Br} + \text{Cl}_2 \rightarrow$ [4]
- (d) (i) Suggest a sequence of reactions for the preparation of $\text{Fe}(\text{CO})_3(\text{diphos})$, given iron metal, CO, diphos ($\text{Ph}_2\text{P-CH}_2\text{-CH}_2\text{-PPh}_2$), and other reagents of your choice.
- (ii) Propose a synthesis for $\text{HMn}(\text{CO})_5$, starting with $\text{Mn}_2(\text{CO})_{10}$ as the source of Mn and other reagents of your choice. [10]
- (e) Select the best choice in each of the following, and briefly justify the reason for your selection.
- Shortest C–O bond: $\text{Ni}(\text{CO})_4$, $[\text{Co}(\text{CO})_4]^-$, $[\text{Fe}(\text{CO})_4]^{2-}$
 - Highest C–O stretching frequency: $\text{Ni}(\text{CO})_3(\text{PF}_3)$, $\text{Ni}(\text{CO})_3(\text{PCl}_3)$, $\text{Ni}(\text{CO})_3(\text{PMe}_3)$ [4]

QUESTION TWO

- (a) The reaction of chloroform with $\text{Co}_2(\text{CO})_8$ yields a compound of formula $\text{Co}_3(\text{CH})(\text{CO})_9$. NMR and IR data indicate the presence of only terminal CO ligands and the presence of a CH group. Propose a structure consistent with the spectra and the correlation of cluster valence electron (CVE) count with structure. [5]
- (b) Give organic fragments isolobal with each of the following:
(i) $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}$ (ii) $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$
(iii) $[\text{Fe}(\text{CO})_2(\text{PPh}_3)]^-$ [3]
- (c) Use Wade's rules to predict the structures of the following:
(i) B_5H_8^- (ii) $\text{Os}_5(\text{CO})_{16}$
(ii) $\text{Os}_6(\text{CO})_{17}[\text{P}(\text{OMe}_3)]_3$ [6]
- (d) (i) Give a definition of a metal cluster.
(ii) What are the two broad classes of metal carbonyl clusters?
(iii) $\text{M}_3(\text{CO})_{12}$ clusters (M = Ru and Os) are unreactive. Give three ways by which they can be converted into more reactive derivatives. [9]
- (e) What are the formulas of the metal carbonyls that are isoelectronic with
(i) $\text{Co}(\text{NO})_3$
(ii) $\text{Fe}(\text{CO})_2(\text{NO})_2$? [2]

QUESTION THREE

- (a) Explain with necessary diagrams the bonding in CO to transition metal atoms with emphasis on the σ -donor and π^* -acceptor functions of the ligand. [4]
- (b) The complex $[\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_3]$ can be used in the catalytic synthesis of n-pentanal from an alkene having one less carbon atom.
(i) Outline the main steps in the mechanism of this process indicating the reaction type of each step (such as oxidative addition) and identifying the catalytic species. [10]
(ii) Increasing the concentration of phosphine in the phosphine-rhodium cycle slows the reaction rate. Explain. [5]
- (c) Using the most appropriate acid-base theory, identify the acids and bases in the following reactions:
(i) $\text{SiO}_2 + \text{Na}_2\text{O} = \text{Na}_2\text{SiO}_3$
(ii) $\text{B}(\text{OR})_3 + \text{NaH} = \text{Na}[\text{HB}(\text{OR})_3]$
(iii) $\text{Cl}_3\text{PO} + \text{Cl}^- = \text{Cl}_4\text{PO}^-$ [6]

QUESTION FOUR

- (a) (i) Why is it difficult to separate lanthanide ions?
(ii) A mixture of lanthanide metal ions was prepared containing Ce^{3+} , Eu^{3+} and Yb^{3+} . To separate the ions, a portion of the solution of the ions was poured through a sulphonated polystyrene ion-exchange resin. The column was then eluted with a dilute solution of H_4EDTA adjusted to pH 8 with ammonia.
(1) Which ion comes out first? Explain.
(2) Suggest another buffer solution that could be used to elute the ions from the column. [9]
- (b) An empty, a half-filled and a completely filled $4f$ electronic level is often said to confer stability on the oxidation state of a lanthanide ion. Cite examples which bear out this statement. [3]
- (c) (i) Use Hund's rules to derive the ground state term of Nd^{3+} .
(ii) Hence determine the magnetic moment, μ . [6]
- (d) What are the main sources of
(i) Thorium, (Th)
(ii) Uranium, (U) [4]
- (e) Work out the number of unpaired electrons in the ions
(i) Gd^{3+}
(ii) Tm^{3+}
(iii) Lu^{2+} [3]

QUESTION FIVE

- (a) Describe the main types of interhalogen compounds giving examples of each. [6]
- (b) Predict the products of the following reactions of interhalogens:
(i) $\text{ClF} + \text{S} \rightarrow$
(ii) $\text{ClF}_3 + \text{SbF}_5 \rightarrow$
(iii) $\text{IF}_5 + \text{CsF} \rightarrow$ [3]
- (c) Given that 1.84 g of IF_3 reacts with 0.93 g of $[(\text{CH}_3)_4\text{N}]\text{F}$ to form a product **X**:
(i) identify **X**
(ii) Use VSEPR model to predict the shapes of
(1) IF_3
(2) the cation in **X**
(3) the anion in **X** [8]
- (d) The interhalogen compound, I_2Cl_6 exists as a dimer in the solid state.
(i) Write a balanced equation for the preparation of this compound. [2]
(ii) I_2Cl_6 undergoes dissociation on warming to room temperature. Write the reaction for the dissociation process. [3]
- (e) Ligand substitution reactions on metal clusters are often found to occur by associative mechanisms, and it is postulated that these occur by initial breaking of an M-M bond, thereby providing an open coordination site for the incoming ligand. If the proposed mechanism is applicable, which would you expect to undergo the fastest exchange with added ^{13}CO ? $\text{Co}_4(\text{CO})_{12}$ or $\text{Ir}_4(\text{CO})_{12}$? Suggest an explanation. [3]

QUESTION SIX

- (a) Indicate with sketches the structures of the following:
- (i) LiCH_3
 - (ii) $\text{Hg}(\text{CH}_3)_2$
 - (iii) $\text{Al}(\text{CH}_3)_3$ [6]
- (b) (i) How is an alkylidetriphenylphosphorane (Wittig reagent) made?
(ii) What is it used for? [4]
- (c) Select the best answer and give the basis for your selection.
- (i) Strongest acid: H_2O , H_2S , H_2Se or H_2Te
 - (ii) Stronger base: NF_3 or NH_3 [4]
- (d) Use the hard and soft acid base (HSAB) theory to predict which of the following pairs of adducts should be the more stable:
- (i) $[\text{Fe}(\text{NMe}_3)_6]^{3+}$ or $[\text{Fe}(\text{SbMe}_3)_6]^{3+}$
 - (ii) BeI_2 or BeF_2 [4]
- (e) (i) Draw the Lewis diagrams for all the species involved in the reaction
$$2\text{HSO}_3\text{F} = \text{H}_2\text{SO}_3\text{F}^+ + \text{SO}_3\text{F}^-$$

(ii) Discuss this equilibrium
- (1) in terms of the solvent-system definition of acids and bases.
 - (2) in terms of the Lewis definition of acids and bases. [7]